ADSORPTION OF Pb (II) USING SHEEP FUR: ISOTHERM, KINETICS AND THERMODYNAMIC STUDIES

ABSTRACT

Sheep fur (SF), a keratinous biomaterial, was used as a low cost adsorbent for removal of Pb(II) from aqueous solution. The sorbent was characterized, where moisture content, pH, bulk density and loss on ignition were determined. The experimental data were analyzed by Langmuir, Freundlich, Temkin and Dubinin Radushkevich model with the Langmuir model showing the best fit. Maximum adsorption capacity of Pb(II) by the SF was 45.46 mg/g. Separation factor R_L was 0.037 indicating a favourable adsorption process. The results also indicated that kinetic data were best described by the pseudo second-order model with a correlation coefficient (R^2) of 0.997. Negative standard Gibb's free energy (ΔG) obtained indicated that the Pb(II) adsorption process was spontaneous and thermodynamically feasible. Fourier Transform Infra-red Spectroscopy (FTIR) analysis confirmed the presence of carboxyl, hydroxyl, amino and sulphur-containing functional groups on the SF.

INTRODUCTION

Rapid industrialization has resulted in serious environmental and health issues causing heavy metals to accumulate in the environment due to increasing demand for goods made by chemical industries [1]. The indiscriminate discharge of pollutants into the environment, using the aquatic system as a sink, is more challenging because heavy metal pollution of the aquatic environment is a severe environmental issue [2]. This frequently decreases the water body's primary and/or secondary uses [3]. Even in small concentrations, these metals are hazardous to both plants and animals.

They are hazardous because they can bioaccumulate, persistent by nature, non-biodegradable and toxic even at low concentrations [4]. When present in higher than necessary concentrations, heavy metals in water have been found to be harmful. Industries are the biggest contributors of pollution in all areas [5]. Heavy metals like lead if overly present in blood above 100 ppb can induce discomfort, mental retardation, brain damage, generate tumour and block haem synthesis. Long-term consumption of lead-contaminated water poses a health concern [6].

Heavy metal contamination in diverse wastewaters have been treated using a variety of techniques, most commonly chemical precipitation (hydroxides, sulfides, etc.), membrane filtration (reverse osmosis, nanofiltration, etc.), electrochemical treatment, solvent extraction, ion exchange, and adsorption. Chemical precipitation and electrochemical treatment are inefficient, especially when the concentration of metal ions in the aqueous solution is between 1 and 100 mg/l, and they also result in a significant amount of sludge that is very challenging to treat. When treating large amounts of wastewaters containing heavy metals at low concentrations, membrane filteration, solvent extraction and ion exchange are prohibitively expensive and cannot be used on a large scale [7].

As a result, the majority of these techniques have certain drawbacks such complicated processes, high costs and high energy use. Due to its simplicity of use and cost-effectiveness, adsorption is regarded as the best solution in these circumstances. Also. Through metabolically driven or physico-chemical modes of uptake, adsorption has recently become a viable option for creating an eco-friendly wastewater treatment method [8].

Based on the capacity of various biological materials to bind metals, adsorption has received interest in the search for innovative methods involving the removal of harmful metals from wastewaters. Because of its effectiveness, efficiency and availability of biomass as a biosorbent [9], adsorption has been shown to have a good potential to replace traditional approaches for the removal of heavy metals [10]. Adsorption as defined by Wang and Chen (2009) is the process of using biological material to remove metal and metalloid species, compounds, and particles from solution [11].

Natural, industrial and agricultural waste are being considered as inexpensive sorption materials. Heavy metals can be removed from aqueous solutions using a variety of biomaterials, including algae, bacteria, mosses, plant materials, agricultural wastes, and keratin biomaterials (hair, feathers, horn, etc) [12].

EXPERIMENTAL METHODS

All the chemicals used in this work were of analytical grade. To prepare the adsorbate, a 1000 mg/L stock solution of Pb(II) was first prepared. It was then diluted to the necessary concentration for each experiment. Prior to starting the adsorption tests, the pH of the solution was adjusted using a combination of sodium hydroxide (0.1M) and nitric acid (0.1M).

Sheep Fur (SF) was obtained from a Fulani village in the Kwali Area Council of the Abuja. The samples of sheep fur were cleaned with detergent, rinsed several times with deionized water, allowed to dry at room temperature and then cut into small pieces. The parameters listed below were used to characterize the furs: moisture content, loss of mass on ignition, pH and bulk density using standard procedures

Adsorption experiment

In a single metal (Pb(II)) aqueous solution, adsorption isotherm investigations were carried out at room temperature while altering the starting metal concentration. A stirrer operating at 250 revolutions per minute was used to agitate a mixture of 50 mL of Pb(II) aqueous solutions and SF at pH 4.0 for three hours. The mixture was filtered and AAS was used to determine the concentration of metal ions in the filtrate.

The concentration of adsorbed metal ions per unit mass of biosorbent is known as the metal uptake (Q, in mg/g), and it was determined using the following equation:

$$Q\ (\text{mg/g}) = \frac{(C_I - C_f) \times V}{W}$$

Where C_i and C_f are the initial and the final concentration of metal ions in the aqueous solution respectively (in mg/L), V is the total volume of the solution (in L) and W is the total amount of biosorbent used (in g).

KINETIC STUDIES

Eleven flasks each containing 50 cm^3 of a specified quantity of Pb (II) ions for the kinetic studies were used. For the various times (10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360 minutes), 0.1 g of SF was added to each of them and stirred individually on a stirrer at room temperature at a speed of 270 rpm. The aqueous and solid phases were separated by filtration and the concentration of metal ions in the resulting aqueous solution was analyzed by AAS after each interval of time.

STUDIES ON THERMODYNAMICS

50 cm^3 of aqueous solutions with known metal ion concentrations were added to 100 cm^3 flasks in order to investigate thermodynamic characteristics. Each of these flasks received an addition of 0.05 g of biosorbent. At room temperature, these flasks were stirred at a speed of 270 rpm using a stirrer. To determine the final metal concentrations, they were allowed to settle, filtered, and the filtrates were examined. At various temperatures, same procedures were repeated.

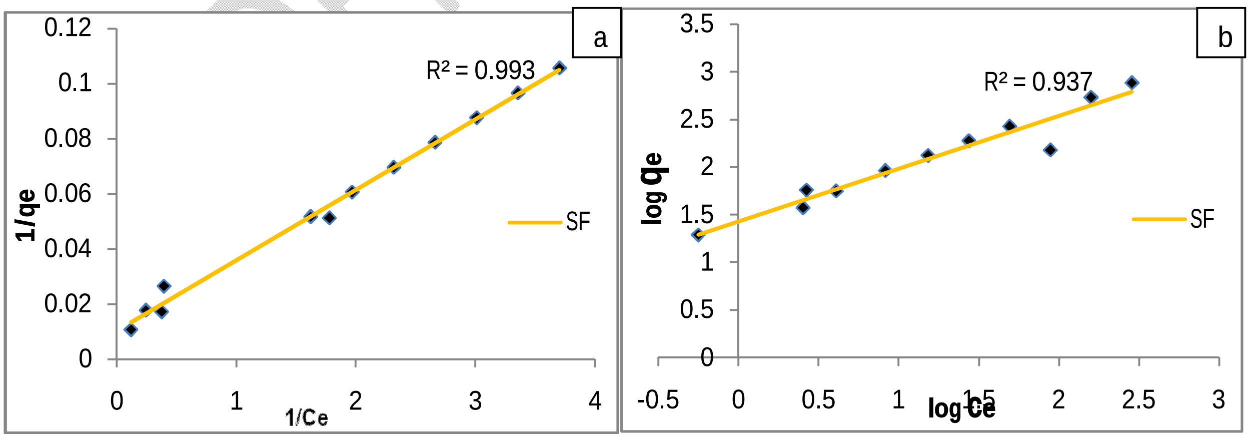
FTIR Analysis

The SHIMADZU FTIR-8400S was used to record FTIR spectra at room temperature at wavenumbers 4000-400cm^{-1}, 45 scans, and a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Table 1: Physico-chemical analysis of SF

Properties	**SF**
pH	8.50
Moisture content (%)	8.01
Loss on ignition (%)	97.89
Bulk density (g/cm^3)	0.0298



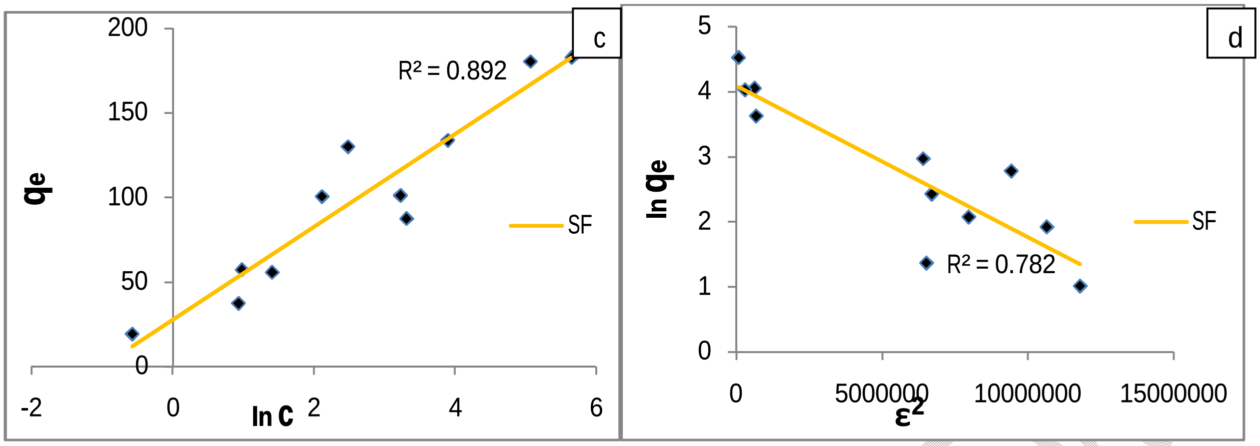


Figure 1: (a) Langmuir, (b) Freundlich, (c)Temkin and (d) D-R isotherm plots for the adsorption of Pb(II) by SF

Table 2: Isotherm parameters for Pb(II) adsorption onto the SF

Langmuir		Freundlich		Temkin		Dubinin Radushkevich	
$q_e = \frac{Q_{max} bC_e}{1 + bC_e}$		$q_e = K_f . C_e^{1/n}$		$q_e = \frac{RT}{b} \ln (A_T C_e)$		$q_e = q_s \exp(-K_{DR} \varepsilon^2$	
Q_{max} (mg/g)	45.46	1/n	0.570	A_T (L/mg)	3.028	q_s (mg/g)	62.93
b (L/mg)	0.500	n	1.754	b_T (KJ/mol)	0.098	K_{DR} (mol^2/KJ^2)	2 x 10^{-7}
R_L	0.037	K_f [mg/g(L/mg)$^{1/n}$]	4.162	B	25.24	E (KJ/mol)	1.581
R^2	0.993	R^2	0.937	R^2	0.892	R^2	0.782

The design of adsorption systems benefits from the analysis of equilibrium adsorption data, which can also be used to assess the effectiveness of various biosorbents under various operational conditions in order to improve the working process. Four isotherm models—Langmuir, Fruendlich, Dubinin-Radushkevich, and Temkin—were used to assess sorption data among the many known isotherm models in order to determine the maximum saturation capacity of SF.

Due to a greater correlation coefficient, the results showed that the Langmuir model better describes the adsorption process of Pb(II). This pattern emerges based on correlation coefficient from the use of these models for SF/Pb(II) data points: Langmuir > Freundlich > Temkin > Dubnin-Radushkevich

Some of the assumptions of the Langmuir model are:

- There are a finite number of energetically identical sites on the solid surface.

- There are no interactions between the adsorbed species, i.e., the amount adsorbed has no bearing on the rate of adsorption.
- When the solid surface reaches saturation, a monolayer forms.
- The number of adsorbed species does not exceed the total number of surface sites, i.e., there is a 1:1 stoichiometry between surface adsorption sites and adsorbate, when the solid surface approaches saturation [13].

Table 2 presents the nonlinear Langmuir model, where Ce = equilibrium concentration of adsorbate (mg/L), qe = quantity of metal adsorbed per unit mass of adsorbent at equilibrium (mg/g), Qmax = maximum absorption capacity (mg/g), and b = Langmuir isotherm constant (L/mg).

The maximum monolayer capacity (Qmax) for Pb(II) was calculated using the Langmuir isotherm model and was found to be 45.46 mg/g; the b value (Langmuir isotherm constant) was 0.500 L/mg, and the R^2 value was 0.993, demonstrating that the sorption data suited the model well.

The separation factor (R_L), which is a dimensionless constant, was determined to ascertain whether the adsorption is favourable. The R_L calculated from Langmuir model was below 1, with value of 0.037 indicating a favourable adsorption process.

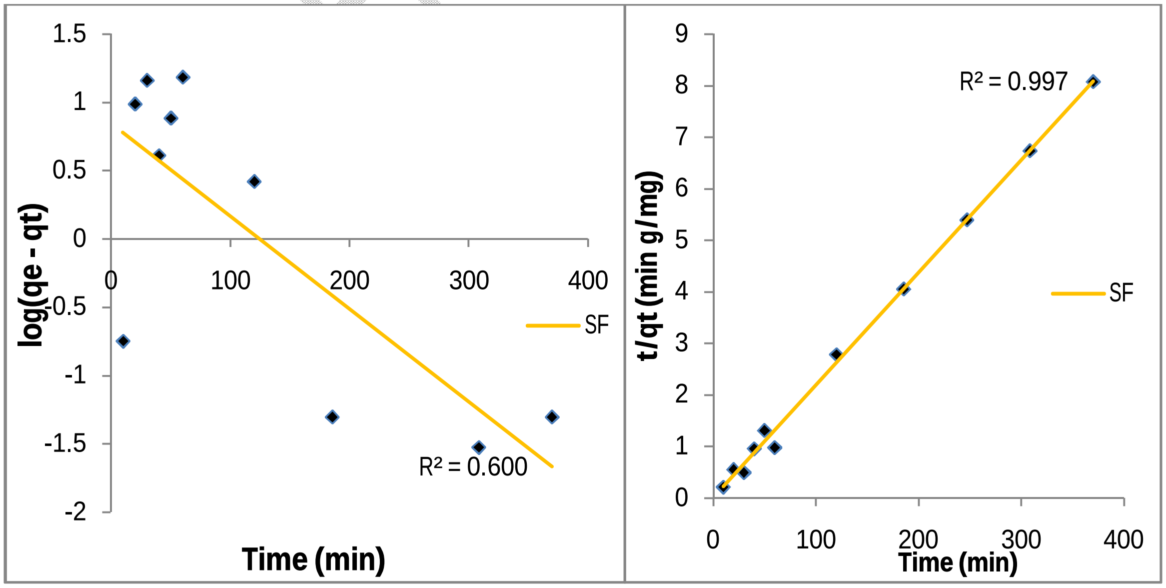


Figure 2: (a) Pseudo First Order and (b) pseudo second order plots for the adsorption of Pb(II) by SF

Table 3: Kinetics parameters for Pb(II) adsorption onto the SF

Pseudo First Order		Pseudo Second Order	
K_1 (min^{-1})	1.15 x 10^{-2}	K_2 (mgg^{-1}min^{-1})	1.79 x 10^{-2}
q_e (mg/g)	10.74	q_e (mg/g)	45.45
q_{exp} (mg/g)	45.85	q_{exp} (mg/g)	45.85
R^2	0.600	R^2	0.997

Adsorption kinetics study is important because it sheds light on the mechanism of adsorption, which includes processes like mass transport, pore diffusion and chemical reactions as potential rate-controlling steps. Pseudo-first order equations and pseudo-second order equations were used to identify the Pb (II) adsorption/SF process.

With a correlation coefficient of 0.997, the pseudo-second order kinetic model provided the best fit to the experimental data. The qe obtained from pseudo-second order was also in good agreement with the experimental data (q_{exp}), as shown in Table 3.

These findings show that, in comparison to pseudo-first order, the adsorption might very well be explained by a pseudo-second order kinetic model at all-time intervals.

Table 4: Thermodynamics parameters for Pb(II) adsorption onto the SF

Conc.	ΔH	ΔS	ΔG (KJ/mol)					
(PPM)	(KJ/mol)	(KJ/mol)	283K	293K	303K	313K	323K	333K
20	7.79	0.0979	-19.92	-20.89	-21.87	-22.85	-23.83	-24.81
30	3.89	0.0839	-19.84	-20.68	-21.52	-22.36	-23.20	-24.04
40	3.50	0.0793	-18.95	-19.74	-20.54	-21.33	-22.12	-22.92

For interpreting adsorption behaviors, thermodynamic studies are important, particularly when it concerns equilibrium of the process [14]. At different temperatures of 10, 20, 30, 40, 50, and 60^{o}C, thermodynamic studies of the adsorption of Pb(II) ions by SF were conducted. The adsorption capacity of adsorbents and the transport/kinetic mechanism of metal adsorption are significantly influenced by temperature. With an increase in temperature, the metal ion's ability for adsorption increased. The relations below can be used to calculate the thermodynamics of the adsorption process utilizing thermodynamic parameters, such as changes in the standard free energy change (ΔG^o), the enthalpy change (ΔH^o), and the entropy change (ΔS^o) associated with the adsorption process:

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\Delta G^o = -RT\ln Kd$

Table 4 shows that all of the adsorption cases have negative (ΔG^o) values, which shows that the metal removal is favoured. The degree of spontaneity is shown to increase with temperature, showing that the capacity of metal ions for spontaneous adsorption along with temperature have a direct relationship. Spontaneity is also seen to decrease with concentration.

Enthalpy change values (ΔH^o) are dependent on initial concentrations. This dependence results from the concentration dependence of K_d, which is utilized to assess thermodynamic parameters. The endothermic nature of the adsorption process is indicated by positive values of ΔH^o obtained at all concentrations.

Entropy change (ΔS^o) values during the adsorption process ranged from 0.0793 to 0.0979 KJ/molK. The positive value of the ΔS^o is a reflection of the increasing randomness at the solid-liquid interface during the adsorption process [15].

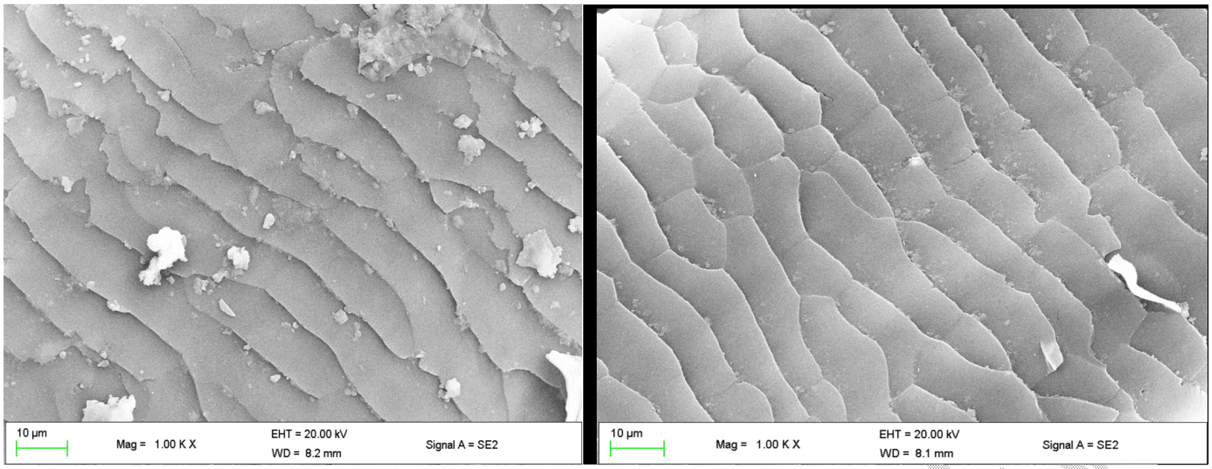


Figure 3: Scanning Electron Micrograph of SF at: (b1) virgin and (b2) loaded at 1000X magnification

Figure 3 shows SEM micrographs of virgin and metal loaded SF that were scanned at 1000x magnifications before and after metal sorption to characterize their surface morphology. From the micrographs, it is evident that there are no significant differences on the surface morphology of SF before and after adsorption, which is advantageous in terms of potential reuse of SF.

The smoother surface of SF following metal adsorption is clearly visible, demonstrating that the superficial layers on the sorbents are closed after adsorption, presumably as a result of the acidic nature of the aqueous solution.

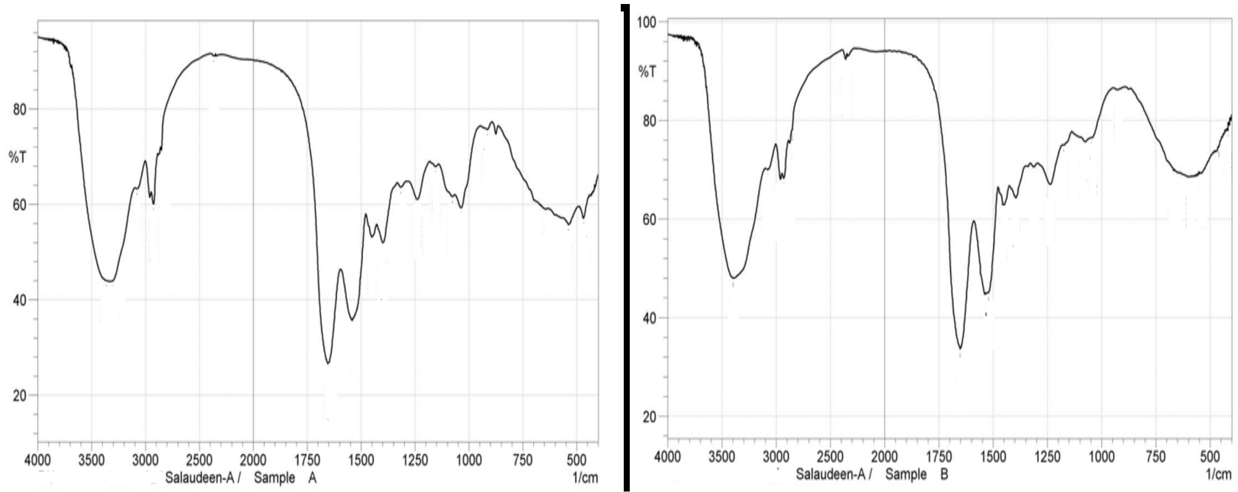


Figure 4: FTIR Spectra of (a) virgin SF and (b) metal loaded SF

FTIR analysis confirmed the presence of carboxyl, hydroxyl, amino and sulphur-containing functional groups in SF with minor changes in the spectra obtained after adsorption. The spectra obtained for the virgin and metal loaded SF are very similar, indicating that the main functional groups did not change significantly during the adsorption process, indicating the possibility of regeneration and re-use.

CONCLUSION

Sheep fur was used as adsorbent for the removal of Pb(II) from aqueous solution. The maximum adsorption capability of SF reached was 45.46 mg/g. Isotherm modeling revealed that the Langmuir model better described the adsorption of Pb(II) on SF as compared to other model used. The negative ΔG^O values indicated the feasibility and spontaneous nature of this process. It could be concluded that SF is a potential and active biosorbent for removal of Pb ions from aqueous solution and industrial waste water.

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